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ADHESIVES

[Setchakuzai]

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Claims

1. Adhesives, characterized by containing polymers that can be obtained from dissolving acrylic monomer-soluble fluorine-containing polymers in acrylic monomers, followed by carrying out polymerization and optionally with formation of an IPN [interpenetrating polymer network].

2. In the adhesives described in Claim 1, the fluorine-containing polymers are vinylidene fluoride copolymers.

Detailed explanation of the invention

Industrial application field

The present invention relates to adhesives having excellent adhesive strength.

Prior art

As adhesives for fluoro-rubber, heretofore epoxy adhesives with excellent adhesive strength have been widely used. However, when such adhesives are subjected to a heat resistance test, for example in boiling water (100°C), peeling occurs in several hours.

Problems to be solved by the invention

The objective of the present invention is to provide adhesives having excellent heat resistance, weatherability, chemical resistance, transparency, strong adhesive strength to various metals, resins, ceramics, woods, etc.

Above all, the objective of the present invention is to provide adhesives with improved adhesive strength when the substrates are fluoro-rubber, acrylic polymer, styrene polymer, etc. in case acrylic monomers permeate in the substrates.

Means to solve the problems

The present invention presents adhesives that are characterized by containing polymers that can be obtained from dissolving acrylic monomer-soluble fluorine-containing polymer in acrylic monomer, followed by carrying out polymerization and optionally with formation of an IPN. By integrating fluorine-containing polymer with acrylic polymer as one body, the above-mentioned problems can be solved.

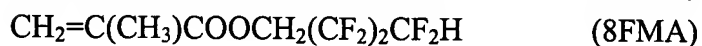
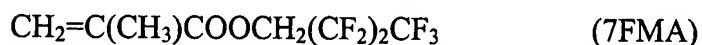
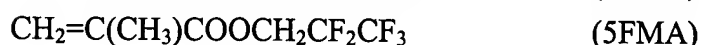
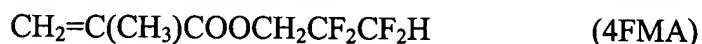
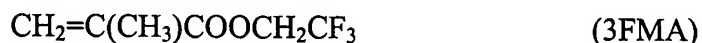
In the present invention fluorine-containing polymers that can be dissolved in acrylic monomers, such as copolymers of vinylidene fluoride, can be used.

Preferable vinylidene fluoride copolymers have a number-average molecular weight of 500-1,000,000 and they can be obtained by copolymerization of vinylidene fluoride with one or more copolymerizable monomers. Representative examples of other copolymerizable monomers include tetrafluoroethylene, chlorotrifluoroethylene, trifluoroethylene, vinyl fluoride, hexafluoropropylene, pentafluoropropylene, hexafluoroisobutene, perfluorocyclobutene, perfluoro(methylcyclopropylene), perfluoroallene, α , β , β -trifluorostyrene, perfluorostyrene, polyfluoroalkyl vinyl ethers (such as perfluoro(methyl vinyl ether), perfluoro(propyl vinyl ether), etc.), poly(fluoroacrylic acid) or an ester thereof, poly(fluorovinyl acetate) or an ester thereof, poly(fluorovinyl ether sulfonic acid), poly(fluorodienes), ethylene, propylene, acrylic acid or an ester thereof, vinyl acetate or an ester thereof. There is no limitation to their content; however, usually 10-60 wt% is preferable. And among these polymers, those having iodine atoms or

bromine atoms in the polymer chain (such as those described in Japanese Kokai Patent Application Nos. Sho 53[1978]-125491 and Sho 59[1984]-20310 and Japanese Kokoku Patent No. Sho 53[1978]-4115) improve polymerization reactivity and thus they are preferable. Further vinylidene fluoride copolymers that are to be contacted with acrylic monomers prepared by crosslinking by routine methods may be used.

Examples of other fluorine-containing copolymers include tetrafluoroethylene-propylene copolymer, tetrafluoroethylene-propylene-vinylidene fluoride ternary copolymer, hexafluoropropylene-ethylene copolymer, fluorovinyl ether-olefin copolymer, fluorophosphazene polymers, etc.

There is no limitation to acrylic monomers in the present invention as long as they can dissolve fluorine-containing polymers and contain mono- or multi-functional groups; preferably they include acrylic acid, methacrylic acid, methyl methacrylate (MMA), ethyl methacrylate (EMA), butyl methacrylate (BMA), 2-hydroxyethyl methacrylate (HEMA), 3-(trimethoxysilyl)propyl methacrylate (MSPM), 2-(phenylphosphoryl)ethyl methacrylate (phenyl-P), 2-hydroxy-3-(β -naphthoxy)propyl methacrylate (HNPM), N-phenyl-N-(2-hydroxy-3-methacryloxy)propylglycine (NPG-GMA), ethylene glycol dimethacrylate (EDMA or 1G), diethylene glycol dimethacrylate (DiEDMA), triethylene glycol dimethacrylate (TriEDMA), 1,4-butanediol dimethacrylate (1,4-BuDMA), 1,3-butanediol dimethacrylate (1,3-BuDMA), 2,2-bis(4-(2-hydroxy-3-methacryloxypropoxy)phenyl)propane (Bis-GMA), 2,2-bis(4-methacryloxyphenyl)propane (BPDMA), 2,2-bis(4-methacryloxyethoxyphenyl)propane (Bis-MEPP), 2,2-bis(4-methacryloxypolyethoxyphenyl)propane (Bis-MPEPP), di(methacryloxyethyl)trimethylhexamethylene diurethane (UDMA), trimethylolpropane trimethacrylate (TMPT),



and the corresponding acrylates and α -fluoro acrylates. One or a mixture of at least two of these compounds may be used and especially MMA and fluorine-containing acrylic monomers are preferable.

In the present invention the above-mentioned fluorine-containing polymers are dissolved in acrylic monomers, and then polymerization is carried out and optionally with formation of an IPN; thereby adhesion can be carried out. However, in this case it is carried out in the presence of polymerization initiators, and optionally a polymerization inhibitor, reducing agent, chain

transfer agent, etc. may be added. In addition to light and heat, polymerization initiators include benzoyl peroxide, azoisobutyronitrile (AIBN), camphorquinone (CQ), 9-fluorenone, tributylborane (TBB), etc.; reducing agents include dimethylaminoethyl methacrylate (DMAEMA), dimethyl-p-toluidine (DMPT), etc.; polymerization inhibitors include such as hydroquinone, hydroquinone methyl ester, etc.; and chain transfer agents include lauryl mercaptan, etc.

An IPN (interpenetrating polymer network) is a polymer formed by mixing two kinds of chain polymers in a liquid state (or solution state), and then one or both polymers are crosslinked so that the molecular chains intertwine mutually.

For IPN formation to proceed, it is necessary to carry out crosslinking. Formation methods include the use of the above-mentioned vinylidene fluoride copolymers that were crosslinked in advance in a routine process (at that time it is preferable to use polymer chain containing iodine atoms or bromine atoms), the use of aforementioned acrylic monomers having at least two functional groups or the use of crosslinking agents, etc.

For the first two methods, those already mentioned may be used. Examples of crosslinking agents that can be used include multifunctional unsaturated compounds such as triallyl isocyanurate, triallyl cyanurate, triacryl formal, triacryl trimellitate, diallyl phthalate, etc. And at this point organic peroxides may be used as radical sources. By forming IPN, the adhesive strength, solvent resistance, etc. can be improved further.

The adhesives of the present invention use monomer solutions of fluorine-containing polymers; therefore the adhesives penetrate into the substrates and as a result strong adhesive strength can be obtained. And the adhesives of the present invention can be used even in a one-liquid form; however, preferably an initiator and reducing agent are separately added to fluorine-containing polymer and acrylic monomer solutions to prepare two separate liquids and the two liquids are mixed immediately prior to use.

In the present invention when polymerization reaction is carried out by heating, it is carried out for example at about 55-100°C for about 10-150 min, and when it is carried out by photopolymerization, for example it is preferable to irradiate with light for several minutes to several tens of minutes. The number-average molecular weight of the polymer obtained by the above-mentioned polymerization is preferably about 1000-300,000.

Why the amount of residual acrylic monomer is very little in the polymers obtained in the present invention is not clear. Especially within the scope that the ratio of fluorine-containing polymer to monomer exceeds one, the amount of residual monomer is almost zero in heating polymerization and in photopolymerization as well, whereas if the polymerization is carried out when poly(methyl methacrylate) is dissolved in methyl methacrylate, the amount of residual monomer is 0.5% with heating polymerization and 2.4% with photopolymerization. Thus

residual monomer cannot be detected in the adhesives containing the polymers of the present invention or the amount detected is very little; therefore they are useful even as adhesives for biomaterials. In addition, the polymers obtained by the present invention can be treated with solvents to form liquids or pastes and then they can be used in the form of liquids and pastes.

If necessary, fillers, catalysts, diluents, coupling agents, etc. may be added to the adhesives of the present invention.

Application examples

In the following, application examples and comparative examples will be used to explain the present invention. The "%" in the examples means "wt%."

Application Example 1

Liquid A: G 801/MMA/BPO = 1/1/0.02 (weight parts)

Liquid B: G 801/MMA/DMPT = 1/1/0.02 (weight parts)

wherein G 801 is Dai-el G 801 (iodine-containing vinylidene fluoride elastic copolymer), MMA is methyl methacrylate, BPO is benzoyl peroxide, and DMPT is dimethyl-p-toluidine.

Cured G 801 was punched to form dumbbell-shaped No. 4 pieces, the central part was cut with a cutter, liquid A was mixed with liquid B (mixing ratio was 1: 1 by weight) and immediately coated on the substrate, and then they [cut pieces] were adhered together. After standing at room temperature for one hour the tensile breaking strength was found to be 82 kg/cm² under an autograph condition of 500 mm/min.

Comparative Example 1

Under the conditions of Application Example 1 an epoxy adhesive was used to carry out adhesion. The tensile breaking strength was found to be 55 kg/cm².

Application Example 2

The central part of 20 x 2 x 70 mm laminar cured G 801 was cut, and similarly the cut pieces were adhered together using liquid A and liquid B having the same compositions as those of Application Example 1. Even after the sample was put in boiling water for 138 h, strong adhesion was exhibited.

Comparative Example 2

Tests of an epoxy adhesive were conducted under the conditions of Application Example 2. The results of the tests indicated that after 6 h the adhesive strength dropped to the extent that breaking occurred with bare hands.

Application Example 3

Two pieces of laminar acrylic plates (10 x 2 x 40 mm) were adhered together with a cross-sectional area of adhesion of 1 cm² using liquid A and liquid B having the same compositions as those of Application Example 1. After standing at room temperature for one hour, pulling under the autograph condition of 500 mm/min was implemented, and breaking occurred at the part of the acrylic plate; thus strong adhesion was exhibited.

Application Example 4

Liquid A: G 801/MMA/1G/TAIC /2.5B/BPO = 1/0.95/0.05/0.04/0.015/0.02 (weight parts)

Liquid B: G 801/MMA/1G/TAIC/2.5B/DMPT = 1/0.95/0.05/0.04/0.015/0.02 (weight parts),

wherein 1G is ethylene glycol dimethacrylate, TAIC is triallyl isocyanurate, and 2.5B is Perhexa 2.5B (Peroxide, Nippon Oil & Fats Co., Ltd.).

Cured G 801 was punched to form dumbbell-shaped No. 4 test pieces, and after the central part was cut with a cutter, liquid A was mixed with liquid B at a mixing ratio of 1: 1 (weight ratio) and the result immediately coated on the surfaces to be adhered together. After standing at room temperature for one hour, heating at 160°C for 10 min was used to polymerize. Then pulling under the autograph condition of 500 mm/min was implemented, and the tensile breaking strength was 96 kg/cm².

Comparative Example 3

An epoxy adhesive was used to carry out adhesion under the conditions of Application Example 4. The tensile breaking strength was 55 kg/cm².